PROCEEDINGS
OF THE
NATIONAL ACADEMY OF SCIENCES
Volume 2 SEPTEMBER 15, 1916 Number 9

THE MECHANISM OF DIFFUSION OF ELECTROLYTES THROUGH ANIMAL MEMBRANES

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Received by the Academy, August 7, 1916

1. In a former paper Loeb and Cattell[1] have shown that embryos of the marine fish *Fundulus* poisoned in a KCl solution until all the hearts stop beating, cannot recover their heart beat when put into H_2O or into a solution of cane sugar, although they will live in such a medium indefinitely; but that they recover in less than a day when put into a salt solution. Eggs which after being poisoned with KCl were kept in H_2O for twelve days without recovering, recovered when put into the solution of an electrolyte.

Conversely it could be shown that when eggs of *Fundulus* are kept for twenty-four hours or longer in distilled water they are poisoned by a solution of potassium salts much more slowly than when the eggs are put into KCl solutions of the same concentration directly from sea water. The washing in distilled water frees the surface layer of the egg membrane from salts and this retards the diffusion of KCl into the egg.

These facts suggested to me the idea that it was impossible for KCl to diffuse through a membrane free from salts and that for such a diffusion two conditions are required: first, a sufficiently high osmotic pressure of the KCl solution, and second, a certain modification of the membrane by an electrolyte, which we will call the 'salt effect.' When the concentration of the KCl solution was sufficiently high, *e.g.*, 3/8m or m/2, the KCl itself might be able to supply this 'salt effect' upon the membranes of washed eggs; but when the solution of KCl was m/8 or below, the solution might not be sufficiently concentrated to supply the 'salt effect' required to allow the diffusion of KCl. This idea was found to be correct.

An m/2 KCl solution caused cessation of the heartbeat of unwashed eggs in less than two hours, and of the washed eggs in about nine hours. An m/8 KCl solution required six days to cause the cessation of the heartbeat in 70% of the eggs previously washed for twenty-four hours in distilled water, while the same solution had the same effect upon unwashed eggs in less than five hours. This difference was due, according to the theory mentioned above, to the presence of the salts of the sea water in the superficial layers of the membrane of the egg. On this assumption it was to be expected that by adding enough sea water to an m/8 KCl solution to bring this solution to a total salt concentration of 3/8m or m/2 the washed eggs should be poisoned much more rapidly. This was found to be the case. While 70% of 'washed' eggs were poisoned by m/8 KCl in H_2O in about six days, the same effect was usually produced in less than one day when the m/8 KCl solution was prepared in m/4 sea water. The same effect was produced by the addition of any salt of Li, Na, or NH_4, and others, to the m/8 KCl solution instead of sea water. Since it might be argued that the addition of a single salt like NaCl might act by merely injuring the membrane and thus increasing its permeability, emphasis should be laid on the fact that these experiments succeeded as well when the 'salt effect' was supplied by balanced solutions like sea water or NaCl + $CaCl_2$ as by non-balanced solutions.

When any of these salts were added to the m/8 KCl solution in a slightly higher concentration than the moderate concentration required to produce the 'salt effect' upon the membrane, the opposite result was noticed: the diffusion of KCl into the egg was again retarded or rendered impossible (antagonistic salt action). Thus the hearts of *Fundulus* embryos were still practically all beating in m/8 KCl made up in m/1 (NaCl + $CaCl_2$ + $MgCl_2$) after eighteen days (when the experiment was discontinued), while they had all stopped beating in less than three days and more than 50% in less than one day in m/8 KCl made up in m/8 (NaCl + $CaCl_2$ + $MgCl_2$). This disposes of the possibility that the general 'salt effect' consists in an increase of the 'permeability' of the membrane through injury by the salt.

The most important fact is that only salts act in this way, namely to accelerate the diffusion of KCl through the membrane when added in moderate concentrations and to retard it again when added in higher concentration. Non-electrolytes, like sugars, glycerin, ethyl or methyl alcohol, and urea, do not show this behavior.

2. The difference in the behavior of electrolytes and non-electrolytes, and the influence of the chemical nature of the salt in this general 'salt

effect' upon the membrane can best be studied in experiments on the recovery of eggs previously poisoned with KCl. Eggs were put directly from sea water into m/2 KCl for twelve hours. These eggs must have contained an excess of KCl, since in this solution all the hearts of unwashed eggs stop beating in less than two hours. The heartbeat was resumed when enough KCl had left the eggs after they had been transferred into the proper solutions. The resumption of the heartbeat became, therefore, an indicator for the rapidity of diffusion of the KCl from the heart into the membrane or the surrounding solution. Since the concentration of KCl was approximately equal in each egg at the beginning of the experiment, the differences in time required for recovery were due to the influence of the outside solution upon the rapidity of the diffusion of KCl from the egg into the membrane. Table I shows the percentage of hearts which recovered from the effects of KCl in various salts of Na, NH_4, and Mg in twenty-four hours. It is obvious that beginning with a limiting lower concentration all the hearts were beating again at that time in all the solutions, although most of the solutions are so poisonous that they would have killed the embryo in a short time had they been able to diffuse in more than traces into the egg. They acted by bringing about a certain modification of the membrane rendering possible the diffusion of the potassium salts.

TABLE 1

	PERCENTAGE OF HEARTS RECOVERING FROM POTASSIUM STANDSTILL IN TWENTY-FOURS IN													
	m/1	m/2	m/4	m/8	m/16	m/32	m/64	m/128	m/256	m/512	m/1024	m/2048	m/4096	H_2O
Sea water		100	100	91	60	50	26	15	45	15	10	25	35	5
$NaCl + CaCl_2$	100	95	100	90	55	55	25	25	5	5				10
NaCl	100	100	100	100	100	90	40	25	15	10				5
NaBr	100	100	100	100	90	75	66	50	35	30	40			5
$NaNO_3$				100	100	70	35	15	10	15	10	0	10	5
Na_2acetate		100	100	100	100	100	85	35	15	0	5	5	0	5
Na_2SO_4		100	100	100	100	90	93	90	81	38	14	5		
$NaHCO_3$				100	100	100	100	75	35	10	5			
Na_2CO_3									35	30	20	20	5	5
Na_2HPO_4					95	100	90	55	50	25	10	14	5	0
Na_3 citrate									95	60	80	30	20	
NH_4Cl		38	72	89	83	77	41	16	15	15				11
$(NH_4)_2SO_4$			45	75	70	75	65	65	50	31	15	10	30	10
$(NH_4)_3$ citrate									80	68	55	25	14	
$MgCl_2$			100	85	95	75	55	25	25	25	15	10	0	5
$MgSO_4$		100	95	70	95	90	80	45	70	30	10	10	15	

The limiting lower concentration to bring about the recovery of 70% or more eggs in twenty-four hours depends in a definite way upon the nature of the anion of all these salts, being for Cl: SO_4: citrate in the ratio of approximately 1 : 4 : 16, as stated in a previous publication.[1]

In time recovery took also place in the solutions below the limiting concentration. In the recovery experiments no antagonistic salt action in noticeable, probably on account of the fact that the decisive boundary is the inner surface of the membrane which receives only traces of the salt from the outside solution, enough to accelerate the diffusion of KCl but not enough to inhibit this process.

Table II shows the behavior of the eggs in twenty-four hours when put into solutions of non-electrolytes. The characteristic influence of increasing concentrations of the solution upon recovery which is so striking in Table I is entirely lacking in this case, m/2 solutions of non-electrolytes acting no better than weaker ones. What little recovery takes place in the solutions of non-electrolytes is 'accidental' and where the figures for recovery are 20% or more, it is probably due to the secondary formation of some acid or alkali through microorganisms or in the embryo. The main fact is that the number of hearts which recovered did *not* increase when the eggs were left for a number of days in the solution of non-electrolytes. When the eggs were transferred from the solution of non-electrolytes to a solution of the proper electrolyte the 'salt effect' and hence the recovery took place.

TABLE II

	PERCENTAGE OF HEARTS WHICH RECOVERED FROM KCl POISONING IN											
	m/1	m/2	m/4	m/8	m/16	m/32	m/64	m/128	m/256	m/512	m/1024	H_2O
Glucose	0	15	10	5	0	0	0	5	0	0	0	15
Cane sugar	14	10	14	20	14	15	15	37	21	32	10	5
Glycerin		20	20	15	11	11	0	15	5	15		10
Methyl alcohol	20	45	25	15	20	10	10	10	20	10	15	10
Ethyl alcohol		5	25	25	35	0	15	5	5	15		10
Urea	5	40	15	10	5	30	10	25	10	20	15	10

Table III illustrates the effect of the cation suggesting an influence of the periodic law. Thus recovery occurs neither in RbCl and CsCl nor in the salts of the alkali earth metals occupying the corresponding position in the next group of the periodic series; namely, Sr and Ba. These cations act by preventing the diffusion of the KCl from the egg for if we transfer the eggs from such a solution to one with an efficient

cation, like Na, they will recover. In experiments on the diffusion of KCl into the egg these salts acted somewhat differently, Mg and especially Ca inhibiting the diffusion.

TABLE III

INFLUENCE OF CATION UPON THE RECOVERY

	PERCENTAGE OF EMBRYOS POISONED BY KCl RECOVERED AFTER TWENTY-FOUR HOURS IN													
	m/1	m/2	m/4	m/8	m/16	m/32	m/64	m/128	m/250	m/512	m/1024	m/2058	m/4096	H_2O
LiCl		30	45	80	60	80	60	30	5	0	10			5
NaCl	90	100	100	100	100	90	40	25	15	10				0
RbCl		0	0	0	5	5	0	1	0	2	0			0
CsCl		5	5	0	0	5	5	0	0	0	0			
$MgCl_2$			100	85	95	75	55	25	25	25	15	10		5
$CaCl_2$				100	100	75	45	20	20					
$SrCl_2$				30	15	30	15	20	0	5	25	0	0	10
$BaCl_2$			5	0	5	10	15	25	10	20	35	10	20	0
NH_4Cl		38	72	89	83	77	41	16	15	15				11
$N(C_2H_5)_4Cl$					100	78	60	23	20	14	5	14	12	10

3. If we wish to formulate a theory of the general 'salt effect' upon the membrane required to make the diffusion of potassium salts possible, we must remember that the conditions for the diffusion of acid into the egg resemble those described for KCl.[2] We know that acids form salts with proteins, which dissociate rather completely into protein ion and the anion of the acid used; while ordinarily the protein molecule (being usually a very weak base and acid) does not dissociate electrolytically to any extent. We can understand the phenomena described in this paper if we assume that the ionization of the proteins of the membrane is the prerequisite for the diffusion of KCl as well as of acid through the membrane. When this ionization of proteins of the membrane is to be brought about by neutral salts, as in the case of the diffusion of KCl, a much higher concentration of the salts is required than when the ionization is caused by acid or base, and the limiting concentration varies with the constitution of the salts. This ionizing effect need not be produced entirely by KCl but, for the 'salt effect,' the KCl can be partly replaced by other neutral salts. When more than a moderate amount of salt is added the ionization of the proteins of the membrane is diminished instead of increased, and the diffusion of KCl may again become as impossible as if a non-electrolyte had been added. A fuller

discussion of the theory will be given in the complete paper. Those cases in which the possibility of diffusion through a membrane was diminished by the addition of too much salt or by a salt with bivalent cation have thus far been singled out for discussion under the heading of antagonistic salt action, but the proof furnished in this paper that the absence of electrolytes acts in a similar but more complete way shows that the case of antagonistic salt action is only a part of the more general problem of the role of electrolytes (or of the ionization of the protein molecules of the membrane) in the diffusion of salts through animal membranes.

Summary and Conclusions.—Our experiments show that for the diffusion of certain electrolytes (potassium salts and acid) through animal membranes besides the osmotic pressure of the electrolyte a second effect is required which we call the 'salt effect' upon the membrane. This consists probably in an ionization of the protein molecules of the membrane. KCl and acid cannot diffuse through a membrane free from salts. The condition necessary for the diffusion of acid and KCl is produced when a trace of acid or a moderate amount of salt is added whereby the protein moleules of the membrane become ionized ('salt effect'). The addition of more salt (whereby the dissociation of the protein molecules of the membrane is diminished and probably other changes are brought about) annihilates this condition again. The latter fact is the special case of antagonistic salt action. The influence of the nature of the salt upon the limiting concentration for the 'salt effect' is stated in the paper.

The nature of the forces by which the ionization of the protein molecules of the membrane may bring about the diffusion of acids and potassium salts (and possibly of electrolytes in general) will be discussed in the main paper.

[1] Loeb, J., these PROCEEDINGS, 1, 473 (1915); Loeb, J., and Cattell, McK., *J. Biol. Chem.*, 23, 41 (1915); Loeb, J., and Wasteneys, H., *Biochem. Zs.*, 31, 430 (1911); 32, 155.

[2] Loeb, J., *J. Biol. Chem.*, 23, 139 (1915); *Science*, 34, 653 (1911); *Biochem. Zs.*, 37, 127 (1912); Loeb, J., and Wasteneys, H., *Biochem. Zs.*, 33, 489 (1911); 39, 167 (1912).

THE ROTATION AND RADIAL VELOCITY OF THE SPIRAL NEBULA N. G. C. 4594

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Received by the Academy, July 18, 1916

The question of the rotation of nebulae has received a considerable amount of attention within recent years. The extreme faintness, however, of these objects, particularly of the spiral nebulae, makes spectroscopic investigation most difficult and laborious; and for only a very few of them are direct photographs available of such quality and separated by such intervals of time as to provide a reasonable hope of detecting changes of position by direct measurement.

In the case of the planetary nebulae Hartmann[1] in 1902 believed that he had found spectroscopic evidence of rotation in the large nebula in Draco and in Struve No. 6. His values, however, are not in accordance with the measures of Campbell and Moore, who recently have published definitive values for several of these nebulae.[2]

In his report for 1913 Wolf[3] stated that the lines in the spectrum of Messier 81, N. G. C. 3031 Ursae Majoris appeared doubly bent near the nucleus, indicating a rotation of 100 km. per sec. near the nucleus, the east side approaching. In *Lowell Observatory Bulletin*, No. 62, Slipher announced the rotation of the nebula which is the subject of this communication, and a few months later gave the numerical data referred to below. Later Wolf[4] mentions attempts to detect rotation in the Ring and Dumb-bell nebulae, but his apparatus was not well adapted to the work.

Van Maanen,[5] from measures of direct photographs, obtained evidence of rotation in Messier 101, together with a possible outward component for the individual knots, which seem to move along the arms of the spiral.

The great lengths of exposure necessary for spectrum work on faint nebulae has suggested the following modification of the slit end of the focal plane spectrograph so that several points in a nebula may be observed simultaneously. In this arrangement the metal jaws of the slit are replaced by a silvered glass plate. This plate and a direct photograph of the nebula taken at the same focus as that at which the spectrograph is to be used are mounted on a comparator, and for each bright spot in the nebula a slit (fig. 1) is cut in the silver film with a dividing attachment, the cut projecting beyond the nebulosity far enough to allow the addition of a comparison spectrum. Spots are chosen so

that their spectra do not overlap. For the comparison spectrum another silvered glass plate is made in which for each continuous cut in the slit-plate there is an interrupted cut (fig. 2), the central portion covering the nebula while the comparison exposure is made on a spark between iron electrodes. This second plate is mounted on a metal frame which swings it almost into contact with the slit-plate when the spark is used. When not in use it is turned out of the way. A dense piece of opal glass between the spark and the slit serves to diffuse the light thoroughly. No projecting lens is employed. It is of course necessary in this arrangement to place the photographic plate at right angles to the axis of the camera.

At the Seventeenth Meeting of the American Astronomical Society, Slipher[6] gave for the nebula N. G. C. 4594 a radial velocity of + 1100 km. per sec., and stated that it has a rotation analogous to that of the planets. He assigns a value of 100 km. per sec. to the linear velocity of rotation at a distance of 20 seconds of arc from the nucleus.

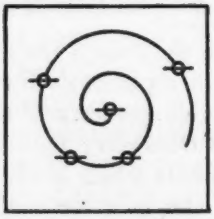


FIG. 1.

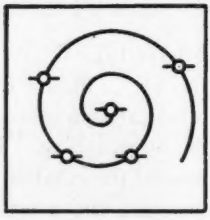


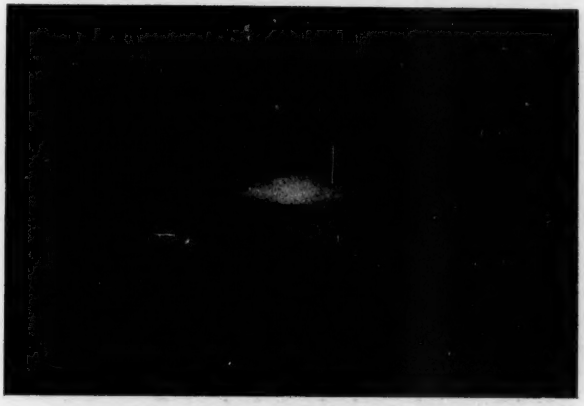
FIG. 2.

A direct photograph (fig. 3) of this nebula shows it to be a spiral seen almost edge on, with the convolutions so nearly concentric that it is not possible to state whether it is of the right or left-handed type. The nebula is crossed by a dark streak which appears to absorb or obstruct the light. This streak seems to lie at the periphery, being possibly an outer ring of cooler material, or perhaps the unilluminated edge of the thin disk of nebulous matter surrounding the brilliant nucleus. With possible differences of temperature in mind, a photograph was taken on a red sensitive plate through a color screen transmitting the region λ 5650–7600, to test for changes of contrast in visual and photographic light. No certain difference was found between this photograph and one taken upon a Seed '23' plate.

A spectrum exposure of 80 hours was made at intervals during March, April, and May, the slit being placed along the major axis of the spindle across the nucleus. Since the nebula is long and narrow a single straight line was in this instance cut in the slit-plate, while the spark plate was

made in such a way that the nebular spectrum was traversed longitudinally by comparison spectra at intervals of 1 mm. The photographic plate accordingly was used in its regular position, and thus a large part of the spectrum was in focus.

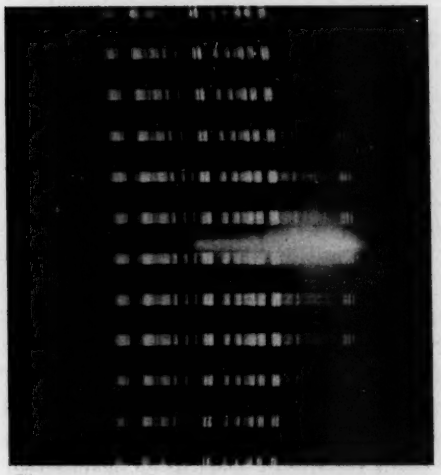
N



E W

FIG. 3.—N. G. C. 4594 EXPOSURE = 2 HOURS. 1 MM = 6.7

E



W

FIG 4.—SPECTRUM OF N. G. C. 4594. EXPOSURE 80 HOURS.

The resulting spectrum (fig. 4) represents approximately the central half of the nebula, and it has been found possible to obtain measures in five spaces ($2\frac{1}{4}$ minutes of arc) on either side of the nucleus. The type is about F5 and seems to be alike in all parts of this nebula. The linear scale of the spectrum is 4.3 mm. from λ 3930 to λ 4950 and most

of the lines measured lie in the more refrangible portion of this region. A valuable check has been furnished by a photograph of the spectrum of the sky and spark taken in the same way as the nebular plate. The results of the measures by Mr. Adams and Miss Burwell are given in Table I. The correction for the earth's motion amounts to -1 km. for the mean epoch of the photograph and has been neglected.

		Adams		Burwell		Mean
		No. lines	Mean *km.*	No. lines	Mean *km.*	Velocity *km.*
West Side	5th space	2	+ 830	4	+ 775	+ 800
	4th space	4	960	6	905	930
	3rd space	4	980	6	930	955
	2d space	6	970	6	970	970
	1st space	6	1155	8	1105	1130
Nucleus		5	1210	7	1190	1200
Adjoining Nucleus		6	1250	7	1275	1260
East Side	1st space	7	1275	7	1275	1275
	2d space	7	1330	9	1350	1340
	3d space	5	1390	5	1395	1390
	4th space	4	+1380	4	1600	1490
	5th space			2	+1630	+1630

These velocities are shown in figure 5, the ordinates being kilometers per second and the abscissae seconds of arc. The velocity curve

$$y = -2.78\,x + 1180$$

was determined by a least squares solution. From this equation we find:

1. The radial velocity of the nebula is + 1180 km., a value in good agreement with that of + 1100 km. found by Slipher.

2. The linear velocity of rotation at a point 2 minutes of arc from the nucleus is over 330 km.

3. Within the limits of accuracy of the measures the change of rotational velocity is linear, although there may be some variation in individual parts of the nebula.

The third result may be interpreted either as indicating that the nebula is rotating as a solid body, or that the material is moving in accordance with a law which will give a linear velocity curve. The latter seems the more probable explanation, since the high velocity is opposed to our conceptions of stability in the case of a rotating solid body. In any event the results seem to be inconsistent with a system involving planetary motion about a central nucleus, since this would require an increase of linear velocity toward the center of the nebula.

If we assume that the rotational component of the internal motion in this nebula is of the same order as that found by van Maanen for Messier 101, we can at once derive a value for the parallax. Van

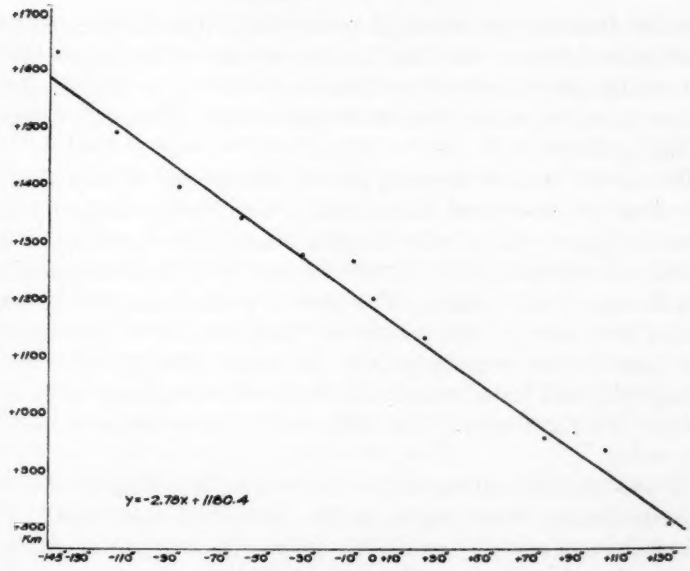


FIG. 5.

Maanen finds for Messier 101 an annual rotational component of 0".022 for a distance of 5′ from the center. Combining this with the rotational velocity of 330 km. per sec. for a distance of 2′ gives 0".00013 for the parallax of N. G. C. 4594. The result is of the same general order as that found by Curtis for spiral nebulae as a class from a discussion of their proper motion.[7]

[1] *Astroph. J.*, **15**, 287 (1902).
[2] *Lick Obs. Bull.*, 278 (1916); *Pub. Astr. Soc. Pac.*, **28**, 119–20 (1916).
[3] *Leipzig, VierteljSchr. astr. Ges.*, **49**, 162 (1914).
[4] *Ibid.*, **50**, 97 (1915).
[5] Van Maanen, these PROCEEDINGS, **2**, 386, July 1916.
[6] *Pop. Astr.*, **23**, 21 (1915).
[7] *Pub. Astr. Soc. Pac.*, **27**, 217 (1915).

A SIMPLE METHOD FOR DETERMINING THE COLORS OF THE STARS

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Received by the Academy, July 24, 1916

Aside from visual estimates, such as those by Müller and Kempf in the *Potsdam Durchmusterung*, three methods of determining the colors of stars have been more or less widely applied. The earliest of

these involves only the use of the spectroscope; the determination of a star's spectral type at once fixes its color, at least within narrow limits. But usually spectroscopic observations are concerned with other physical factors and we ordinarily think of them as only incidentally determinations of color.

The second method depends upon a comparison of photographic and visual or photovisual[1] magnitudes. A red star, owing to a deficiency of light of shorter wave-lengths, makes little impression on the ordinary photographic plate. It will therefore be faint photographically even though visually bright. The light of a white star, on the other hand, affects strongly both the eye and the plate, and its photographic and visual brightness are essentially the same. The difference in the photographic and visual magnitudes is therefore frequently used as a measure of a star's color. This difference is commonly known as the color-index.

The third method determines the color of stars by finding the effective or predominating wave-lengths in the light which they emit.[2] The observations are made by means of a coarse objective grating attached to the end of the telescope. The central diffraction image of each star in the field will have adjoining it on either side tiny images of the first-order spectra. For a red star the blue ends of the spectral images will be weak; the distance separating the points of maximum photographic density is accordingly greater than for a bluer object. From the observed value of this distance the wave-length for the point of maximum density can be calculated. The result is the effective wave-length.

Since spectral type is determined mainly by the number, intensity, and position of the Fraunhofer lines, its relation to color, which depends upon the distribution of intensity in the continuous spectrum background, is not necessarily constant. Thus stars of the same type show differences in color whose origin may be traced to differences in their intrinsic luminosity or absolute magnitude; and any selective absorption or scattering of light during its passage through space must also introduce an element into the star's color which escapes a determination based upon spectral classification.[3] The first method, therefore, does not necessarily give exact values of the color. Moreover, it cannot be used for very faint stars.

The second method is free from the objections attached to the first, but it is not always easy of application. Both the photographic and photovisual magnitudes must be known on the absolute scale. Aside from the difficulties arising from systematic errors in the slope of the scales, there are others, connected with the determination of their zero

points, which at present are likely to prove troublesome. With care satisfactory results can be obtained, but the operation is tedious at best, and the uncertainties are greatest for just those objects whose colors we should like most to know—the faint stars.

The third method, although spectroscopic in character, gives real values of the color, and not merely the spectral type. It is also free from the zero-point and scale errors which complicate precise determinations of the color-index; and although subject to its own peculiar errors, these do not seem to be very serious. The chief objection is that the method is wasteful of light, the limiting magnitude for the determination of effective wave-lengths being about three magnitudes less than that for direct photography.[2] If a large telescope is to be used, the size and weight of the objective grating are also objectionable and make it difficult to pass quickly from the determination of effective wave-lengths to other kinds of observational work.

The following method seems to offer some advantages, and has also the merit of simplicity and convenience. The limiting magnitude to which it can be applied should be about the same as that for which photovisual magnitudes can be determined. It consists simply in determining the ratio of exposure-times necessary to produce photographic and photovisual, or more briefly blue and yellow, images of the same size. For convenience, and also as a matter of precision, the images should be on the same plate. An isochromatic plate exposed behind a yellow filter registers the yellow image as usual. The same plate used without filter gives the blue image. This will include to some extent the effect of the longer wave-lengths, but owing to the relatively small sensitiveness of the isochromatic plate to the yellow and orange rays, the shorter wave-lengths will still be of predominating influence.

In the simplest case there will be for each star one yellow image and a series of three or four blue images, with the exposure times for the latter increasing in geometrical progression—as a constant ratio, 2 seems to be the most convenient. The diameters of the blue images, or their scale readings,[4] are plotted against the logarithm of the exposure, and from the nearly linear curve thus derived can be read the exposure time for a blue image of the same size as the yellow image. The ratio of the interpolated exposure to that which produced the yellow image—the exposure ratio—compared with similar ratios for stars of known color, gives at once the color-index or color-class.[3]

Various modifications necessary to meet special conditions immediately suggest themselves; but whatever the details, consideration should

be given to the following points: First, if there are differences of gradation between the blue and yellow images, the exposure-ratios of bright and faint stars of the same color will be different. In other words, the ratios will depend upon the size of the images. The matter is easily investigated by observing repeatedly the same stars with different apertures and exposure times; the variation of exposure-ratio with the size of image can thus be determined. In practice it will be advantageous, wherever possible, to adjust exposure and aperture so that the resulting yellow image is of a standard size. Preliminary tests indicate that the systematic gradation difference for the blue and yellow images is small. Small deviations from the standard image are therefore of no consequence, and larger differences are readily taken into account in the reductions.

Second, atmospheric extinction reduces the intensity of blue light more than that of yellow and therefore modifies the exposure-ratio. Although the effect enters differentially, its influence is appreciable, except for small zenith distances. Tables of corrections can be derived by determining the exposure-ratio for the same star at different zenith distances.

Third, care should be taken to bring the plates into equilibrium with the atmospheric conditions before beginning the exposures; otherwise the absorption of moisture during the exposure may introduce variations of sensitiveness and gradation which are capable of influencing seriously the results.

No extensive test of the method has yet been made, but it has been tried sufficiently to demonstrate its practicability. About 40 plates, mainly of individual bright stars, were exposed on three successive nights, two or more plates being obtained on each of 10 different stars. Two yellow and five blue exposures were made on each plate; further three exposures through a filter transmitting to the violet of λ 4000 were also added in each case in order to test the precision of results derived from different regions of the spectrum. To avoid gradation errors, the apertures and exposure times were adjusted so that the images differ little from a standard size.

For the plate and filter used the exposure ratio of blue to yellow varies from about $\frac{1}{8}$ to $\frac{1}{3}$ for spectral types A to M. That of blue to ultra-violet would be a much smaller quantity but for the fact that the large exposure factor of the ultra-violet filter was offset by a change in the aperture—the exposures for blue and yellow always being made through a wire-gauze screen absorbing about 3 magnitudes.

PLATE	DATE	HOUR ANGLE	EXPOSURE-RATIOS	
			Blue/Yellow	Blue/Violet
P 3138	1916, June 25	25°W	0.168	0.496
3150	26	1E	0.156	0.542
3163	27	27E	0.178	0.558
3167	27	6E	0.180	0.595
3171	27	15W	0.158	0.600
3173	27	37W	0.164	0.533
3177	27	58W	0.172	0.547
Mean			0.168	0.553
Average deviation from mean			±0.007	±0.027
Change in ratio for 0.1 spectrum interval			0.004	0.014
Spectrum interval corresponding to average deviation			±0.180	±0.190

From the accordance of results for the same star, derived mainly upon different nights, it is found that the average deviation in the exposure-ratio from a single plate corresponds to about 0.2 of a spectrum interval, or 0.08 mag. in the color-index. The greater redness of stars of high luminosity, spectral type remaining the same, is easily seen in the results from even a single plate. The precision seems to be the same whether the yellow or the violet is used for comparison with the blue. As none of the results have yet been corrected for atmospheric extinction, the average deviation includes the effect of this disturbing factor. For illustration the results for seven plates on one of the stars, 72 *w* Herculis, are given in the table.

[1] Photovisual magnitudes express the visual brightness of a star, but are determined photographically. The procedure is the same as for the determination of photographic magnitudes, except that an isochromatic plate combined with a yellow filter is used instead of the ordinary photographic plate.

[2] See for example Hertzsprung, *Mt. Wilson Contr.*, No. 100; *Astroph. J.*, **42**, 92 (1915).

[3] These PROCEEDINGS, 1, 481 (1915).

[4] *Mt. Wilson Contr.*, No. 80, 19; *Astroph. J.*, 39, 325 (1914).

STUDIES OF MAGNITUDES IN STAR CLUSTERS, III. THE COLORS OF THE BRIGHTER STARS IN FOUR GLOBULAR SYSTEMS

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Received by the Academy, August 3, 1916

In a former communication dealing with the probable sequence of spectral types in stellar development[1] it was shown that the brightest stars in the great Hercules cluster are of the redder spectral types, while

among the fainter magnitudes blue stars were conspicuously predominant. Since all the stars of the cluster are at sensibly the same distance from the earth, the apparent difference in brightness between red and blue stars represents an actual characteristic of the brighter objects of the system. This result, however, is not in harmony with the relations heretofore found between color and intrinsic brightness in the less condensed bright clusters and in other selected groups of stars, and it is of importance to seek verification of the phenomenon in additional globular clusters. If it is proved that in these remote, gigantic stellar systems the most luminous objects are chiefly of the redder, low-temperature spectral types, and consequently of very great dimensions relative to the thousands of other stars each cluster contains, the result may have a significant bearing on theories of the evolution of stars. For instance, a satisfactory hypothesis of the evolutionary sequence of spectral and color classes would need to account explicitly for the ancestral relationships of these extremely voluminous second-type (red) stars and the comparatively small bodies of the bluer types.

Measures of the magnitudes and color indices are now available for stars in three other globular clusters. For none of them is the work completed in all its detail, but the preliminary values, taken in conjunction with final results for the Hercules cluster, are sufficiently definite to justify a report regarding the present problem. The observational material and the final discussion will appear in extended form in the *Contributions from the Mount Wilson Solar Observatory*.

The names of the clusters and their positions for the epoch 1900.0 are given in Table I.

TABLE I

DESIGNATION			RIGHT ASCENSION	DECLINATION	GALACTIC LATITUDE	GALACTIC LONGITUDE
Messier	3.....	N.G.C.5272	$13^h\ 38^m$	+28°53′	8°	+77°
	5.....	5904	15 13	+ 2 27	333	+45
	13.....	6205	16 38	+36 39	26	+40
	15.....	7078	21 25	+11 44	33	−29

A number of stars that undergo periodic light variations have been found in these clusters. Such objects were avoided in collecting the results of which a summary appears in Table II. The inclusion of the variables would scarcely change the averages, however, for the plates were taken in pairs and only extremely rapid light changes could enter as systematic errors in the colors. Stars near the center were also omitted from the present treatment in order to avoid possible errors similar to those suspected for the dense central part of Messier 13.[2]

The tabulation of the material needs no general explanation. The photographs now available for Messier 3 do not give a large interval of photovisual magnitude, and consequently, in order to test for the presence of blue stars in this cluster, recourse was had to the short period variable stars. The last average, then, depends entirely on the colors deduced for a number of these variables[3] and, representing a group that is probably peculiar for blueness, is entitled to diminished weight.

The data in Table II show that in these four clusters the average color index is decidedly larger for the brighter stars. Not only is this true in the averages but a detailed examination of the magnitudes involved shows that with few exceptions relatively high luminosity is always accompanied by greater redness. (The exceptions may indicate real anomalies among the members of the cluster, or may be due to the superposed non-cluster stars.) Preliminary consideration of the colors and magnitudes in three additional globular clusters—Messier 4, 9 and 14—shows that the same relation holds for them as that deduced numerically in Table II.

The condition clearly indicated by the above results is that the total light emission of the bluer stars (small color indices), for which the surface temperature is presumably in excess of 10,000 degrees Centigrade, is less than that of many of the redder stars (large color indices),

TABLE II

AVERAGE MAGNITUDES AND COLORS IN FOUR GLOBULAR CLUSTERS

PHOTOVISUAL MAGNITUDE	AVERAGE COLOR-INDEX	NUMBER OF STARS	PHOTOVISUAL MAGNITUDE	AVERAGE COLOR-INDEX	NUMBER OF STARS
Messier 3			*Messier 13*		
12.71	+1.34	10	12.28	+1.28	13
13.34	+1.16	10	13.00	+0.92	23
13.91	+0.88	10	13.50	+0.96	23
14.24	+0.88	9	14.10	+0.73	76
14.51	+0.71	10	14.70	+0.65	110
14.78	+0.73	11	15.30	+0.39	222
(15.20	+0.05	14)	15.70	+0.34	27
			16.45	+0.32	28
Messier 5			*Messier 15*		
12.46	+1.52	6	13.04	+1.35	6
12.93	+1.22	6	13.52	+1.17	7
13.24	+1.20	6	14.19	+0.83	7
13.66	+1.02	6	14.87	+0.86	7
14.42	+0.59	6	15.18	+0.68	7
14.72	+0.44	7	15.54	+0.42	7
14.83	+0.29	7	15.65	+0.32	6

with surface temperatures but half as much. But the light emission per unit area is much less for red stars than for blue. The obvious conclusion is, therefore, that in all these clusters, and probably in all globular clusters, the volumes of the bright red stars are very great in comparison with the stars that are fainter and relatively blue.

[1] These PROCEEDINGS, 2, 12 (1916).
[2] *Mt. Wilson Contr.*, No. 116, Sections IV and VIII (1916).
[3] *Publ. Astr. Soc. Pac.*, No. 163, April 1916.

THE EFFECT OF AN ELECTRIC FIELD ON THE LINES OF LITHIUM AND CALCIUM

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Received by the Academy, August 10, 1916

During the last three years a great deal of work has been done on the electric decomposition of spectral lines. Stark[1] examined the effect in canal rays, subjected to a strong auxiliary field, and Lo Surdo[2] photographed the light immediately in front of the cathode, where the luminosity of the negative glow and the sudden fall of potential fulfilled the required conditions. Hydrogen and helium have been examined by both methods and Stark has investigated the transverse effects for lithium, mercury, and a number of other elements. So far, only H, He, and Li have shown large effects, and the results found for H and He by the two methods differ considerably.

In spite of the great number of data accumulated by Stark, Lo Surdo, and their co-workers since the discovery of the electric effect, the work in this important field is only begun and offers great opportunities for further work. The apparatus used by Stark is very difficult to construct and needs the constant services of a skilled glass blower. Moreover, Stark has already examined most of the more promising elements. The method of Lo Surdo is very simple and has been applied, so far, only to hydrogen and helium. A survey of a number of elements was therefore made with the Lo Surdo form of apparatus, under low dispersion, and in the course of the work some new and interesting results were obtained with calcium and lithium.

A full description of the apparatus used will be published in the *Astrophysical Journal*, but it was essentially of the Lo Surdo form. The tube had an internal diameter of 6 mm. and a length of 20 cm. The discharge from an induction coil was used, rectified by a valve tube. The spectrum was photographed with a three prism, quartz and ultra-

violet glass, spectroscope which gave a dispersion of 1 mm. = 18 A. U. at Hy, and 1 mm. = 12 A. U. at the H and K lines.

Lithium and calcium were examined, both for the longitudinal and transverse effects, and the results are given below in tables I and II. With both elements the spectra were obtained by covering the cathode with a thin layer of the chloride, which gave the characteristic spectrum of the metal under the bombardment of the anode rays. The tubes were filled with hydrogen, and the field strength was determined for every plate by measuring the separation of the outer components of Hy and comparing it with Stark's results. The field strength was about 25,000 volts per cm. close to the cathode. In the following tables the numbers marked + indicate components to the red, − to the violet.

TABLE I

LITHIUM.

Transverse effect for 20,000 volts per centimeter

λ IN A	COMPONENTS POLAR PARALLEL	INT.	COMPONENT POLAR PERPENDICULAR	INT.	REMARKS
4602.37	+1.00	8	+0.48	8	
	−2.48	6	−2.00	6	
4132.93	+2.26	2	+1.78	2	
	−0.18	5	−0.18	5	Unpolarized
	−3.10	1	−2.24	1	
	Longitudinal effect for 20,000 volts per centimeter				
4602.37	+0.57	8	+0.34	6	
	−2.01	6	−1.53	3	
4132.93	+1.16	1	+0.77	1	
	−0.26	5	−0.26	5	Unpolarized
	−1.99	0	−1.50	0	

TABLE II

CALCIUM H AND K

Transverse effect for 20,000 volts per centimeter

λ IN A	COMPONENTS POLAR PARALLEL	INT.	COMPONENTS POLAR PERPENDICULAR	INT.	REMARKS
3968.63	+0.22	6	+0.16	6	Unpolarized
	−0.86	2	−0.74	2	
3933.83	+0.22	9	+0.22	9	Unpolarized
	−0.92	3	−0.74	3	
	Longitudinal effect for 20,000 volts per centimeter				
3968.63	+1.27	3	+1.23	3	Unpolarized
	+0.01	8	−0.02	8	Unpolarized
	−1.17	0	−1.11	0	Unpolarized
3933.83	+1.42	4	+1.38	4	Unpolarized
	+0.06	9	−0.02	9	Unpolarized
	−1.30	1	−1.26	1	Unpolarized

It is interesting to find that the lithium lines λ4602 and λ4132 show polarized components in the longitudinal effect. The longitudinal effects in hydrogen and helium, the only ones investigated up to this time, had given unpolarized components.

Previously, only the diffuse series of elements had shown large electric effects which makes the calcium results most unexpected. H and K belong to a principle pair series and the lines of the diffuse series at λλ4457, 4435, and 4425 show no effect at all, under low dispersion.

A full account of this investigation will be published shortly in the *Astrophysical Journal*.

[1] J. Stark, *Ann. Physik*, 43, 965 (1914); J. Stark and G. Wendt, *Ibid.*, 43, 983 (1914) J. Stark and H. Kirschbaum, *Ibid.*, 43, 991 and 1017 (1914); J. Stark, *Ibid*, 48, 193 (1915).
[2] A. Lo Surdo, *Roma, Rend. Acc. Linci*, 23, 1st. sem., 82, 143, 252, 326 (1914).

A PROOF OF WHITE'S PORISM

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Received by the Academy, August 8, 1916

The interesting theorem of Professor White[1] to the effect that *if two cubic curves in space admit a configuration* Δ_7—i.e., *seven points of the one and seven planes of the other such that each of the points is on three of the planes and each of the planes is on three of the points—then they admit* ∞^1 *such configurations* furnishes perhaps the only important generalization of the Poncelet polygons.[2] Analytically expressed the theorem states that if for a (3, 3) form $F(\lambda,\mu)$ there exists a set of seven parameters λ and seven parameters μ such that $F = 0$ for each λ together with three μ's and for each μ together with three λ's, then there exists ∞^1 such sets Δ_7.

The published proof of this theorem fails owing to an error of enumeration.[3] This error, originally overlooked by Professor White and myself, was noted subsequently by him. That however the theorem itself is true can be shown as follows.

Let $G(\lambda_1, \lambda_2) = 0$ be the condition that distinct values λ_1, λ_2 determine in $F(\lambda, \mu) = 0$ the same value of μ. Then G is a symmetrical (6, 6) form. If $F(\lambda, \mu)$ has a Δ_7, the seven λ's constitute an involutorial set of G, i.e., a set such that any two of the λ's satisfy $G = 0$. Conversely if G has an involutorial set, then $F(\lambda, \mu)$ has a Δ_7. For if λ_1 and any one of $\lambda_2, \ldots, \lambda_7$ satisfy $G = 0$ then, since λ_1 can determine in $F = 0$ at most three μ's, λ_1 must be associated with three pairs of the remaining λ's in such a way that each pair determines with λ_1 a common value μ.

Thus at most seven μ's can be determined by the seven λ's. If however G has one involutorial set, it has ∞^1 such sets.[4] If therefore F admits one Δ_7, it must admit ∞^1 Δ_7's.

[1] A variable system of sevens on two twisted cubic curves, these PROCEEDINGS, 2, 337 (1916).

[2] In the sense that other analogous porisms can be based on the properties of an algebraic (2, 2) form.

[3] The number of poristic forms of the special type which factor into three bilinear forms was estimated at ∞^3 instead of ∞^5.

[4] Coble, Symmetric binary forms and involutions, *Amer. J. Math.*, 31, 189.

A CONTRIBUTION TO THE PETROGRAPHY OF THE PHILIPPINE ISLANDS

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Received by the Academy, August 10, 1916

A very large part of the volcanic rocks of the Philippine Islands occur as tuff-breccias with flows and dikes of massive lava, and a very great area of country is covered with vegetation, so that it will be many years before anything like a thorough knowledge of the igneous rocks of the region will be acquired. Fragmentary contributions to the petrography of the islands are the most that may be expected for some time. Already it is known that the principal volcanic rocks are andesites with much fewer basalts and dacites, and almost no rhyolites. A short visit to Luzon in 1910 enabled one of us to study the collections in the Mining Department of the Bureau of Science [Iddings, J. P., *Philippine J. Sci.*, 5, 155, 1910,] and to collect specimens from some of the more accessible localities on the island. From these specimens the accompanying chemical analyses have been made by Dr. Morley.

The first three analyses are from basaltic lavas having andesitic characters. The rocks are porphyritic with andesitic habit to the groundmass and a variable amount of modal olivine, which is present in the rocks from Antipolo and Taal, but does not appear in the specimen from Mayon which was analyzed, though it occurs in other lava from the same volcano. The normative plagioclase in each case is labradorite.

The basalt from Antipolo, anal. 1, is massive lava from near the waterfall. It is magnophyric and seriate porphyritic with phenocrysts of labradorite and smaller ones of olivine. The groundmass consists of prismoid and anhedral feldspar, anhedral pyroxene and euhedral

magnetite. The norm contains a small amount of quartz, no olivine, and plagioclase which is approximately $Ab_2 An_3$.

The basalt from the south base of Taal volcano, anal. 2, is massive lava on the shore of the lake which surrounds the volcano, and is overlaid by tuffs from more recent eruptions. It has small phenocrysts of plagioclase, augite and olivine, and has more mafic minerals than the rock from Antipolo, but the feldspar is less calcic. The rock is transitional to andose.

The lava from Mayon volcano, anal. 3, is labradorite-andesite, with augite and hypersthene and without noticeable olivine. The norm contains 5% of quartz, but the rock is hessose, closely similar to the basalts from Taal and Antipolo. Other lavas from Mayon contain olivine.

The rock from Benguet Road, anal. 4, is holocrystalline hornblende-andesite or andesite-porphyry, slightly altered. The phenocrysts of plagioclase are zonal with alternating shells which differ in composition, more or less calcic. The hornblende is brownish green, in part altered to chlorite, epidote and calcite. The rock is intruded in andesitic breccias and lavas. The hornblende-andesite from Olongapo, anal. 5, is seriate magnophyric with phenocrysts of zonal plagioclase with alternating zones differing in composition as in the rock from Benguet Road, the outermost zone being strongly calcic instead of strongly sodic as is commonly the case. The hornblende is brown with black border, and opaque paramorphs of hornblende are abundant.

The dacite from Corregidor Island in Manila Bay, anal. 6, is a dense white porphyry forming a large massive body on the sea coast near the landing. It is dopatic and seriate mediophyric, with phenocrysts of glassy plagioclase, quartz and biotite. The groundmass is holocrystalline and seriate microporphyritic, consisting of minute phenocrysts of prismoid plagioclase and abundant microscopic euhedral bipyramidal quartzes in a microcrystalline matrix which besides quartz and alkalic feldspar must contain some kaolin, judging from the chemical analysis and norm, for there is 5% of normative corundum, a large amount of normative quartz and 2.5% of water. The calculated kaolin is 13% which is probably more than is actually present, as some of the normative corundum and water belongs to the modal biotite. The rock is alsbachose, and is the most siliceous volcanic rock from the Philippines so far analyzed. It is interesting to note that the volcanic rocks in these islands are like many in Japan and in western America.

CHEMICAL ANALYSES OF ROCKS FROM LUZON, P. I.

	1	2	3	4	5	6
SiO_2	50.54	52.33	53.06	58.54	60.13	72.68
Al_2O_3	21.63	17.18	19.68	16.79	17.51	15.77
Fe_2O_3	3.64	3.51	3.24	1.89	3.25	0.65
FeO	4.22	5.73	4.94	3.33	0.91	0.21
MgO	3.06	5.30	3.64	3.27	3.35	0.41
CaO	10.47	10.71	9.41	7.25	6.54	1.66
Na_2O	2.88	3.17	3.24	3.76	3.78	3.26
K_2O	1.57	0.94	0.94	1.62	0.77	2.19
H_2O-	0.19	0.00	0.01	0.04	1.45	1.18
H_2O+	0.72	0.38	0.06	1.24	0.90	1.38
TiO_2	0.34	0.31	0.77	0.70	0.44	0.09
P_2O_5	0.24	0.22	0.33	0.66	0.68	0.22
CO_2	0.04	0.02	0.00	0.69	0.02	0.00
ZrO_2	0.00	0.00	0.00	0.01	0.00	0.00
Cl	0.08	0.08	0.08	0.04	0.09	0.02
F	0.02	0.05	0.07	0.05	0.02	0.01
S	0.01	0.03	0.03	0.04	0.02	0.05
Cr_2O_3	0.01	0.01	0.00	0.01	0.00	0.00
MnO	0.17	0.24	0.59	0.13	0.27	0.16
BaO	0.05	0.07	0.06	0.04	0.03	0.02
SrO	0.04	0.03	0.02	0.01	0.01	0.03
	99.92	100.31	100.17	100.31	100.17	99.99
			Norms			
q	0.90	0.96	4.98	11.94	18.00	41.46
or	9.45	5.56	5.56	9.45	5.00	12.79
ab	24.63	27.25	27.25	31.96	31.96	27.77
an	41.14	29.75	36.42	24.19	27.52	7.51
c					0.31	5.30
di	8.34	18.27	6.80	5.81		
hy	8.00	11.82	11.85	8.97	8.40	1.00
mt	5.34	5.10	4.64	2.78	2.78	0.93
il	0.61	0.61	1.52	1.37	0.76	0.15
hm					1.44	
ap	0.34	0.34	0.67	1.68	1.68	0.34
etc	1.16	0.67	0.33	2.17	2.54	2.69
	99.91	100.33	100.02	100.32	100.39	99.94

1. Basalt, hessose, II.5.4.4. Antipolo.
2. Basalt, andose-hessose, II (III).5.(3)4.4'. Taal volcano.
3. Labradorite-andesite, hessose, II,'5.'4.4'. Mayon volcano.
4. Hornblende-andesite, tonalose, II.4'.3.4. Benguet road.
5. Hornblende-andesite, placerose-tonalose, (I) II.4.3'.4(5), Olongapo.
6. Dacite, alsbachose, I.3.2.4. Corregidor Island.

SALT ANTAGONISM IN GELATINE

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Received by the Academy, July 28, 1916

In studying the effects of electrolytes on living organisms Loeb[1] has distinguished two groups of salt antagonisms. To the first belongs the antagonism between NaCl and $CaCl_2$. Here the antagonism is between a monovalent salt and a salt with a strong (bivalent or trivalent) cation. The antagonistic effect increases with the valence of the cation. To the second group belongs the inhibition of the toxic action of KCl on the eggs of *Fundulus* by means of sodium salts, the sulphate and citrate being the most effective. In this second group the antagonism is between a monovalent salt and a salt with a strong (bivalent or trivalent) anion, the effect increasing with the valence of the anion.

A recent explanation of the first kind of antagonism has been presented by Clowes,[2] who assumes that NaCl has a more strongly adsorbed anion and is therefore able to antagonize more strongly adsorbed cations (like Ca). His general conclusion is that electrolytes with a more strongly adsorbed anion are able to antagonize electrolytes with a more strongly adsorbed cation. No explanation is given of antagonism between monovalent salts and salts with strong anions (like Na_2SO_4).

From experiments on gelatine the writer has formulated a hypothesis by which both groups of antagonism may be explained. According to this hypothesis (in many respects similar to that of Clowes) electrolytes with a more strongly adsorbed cation should antagonize electrolytes with a more strongly adsorbed anion, *and in the case of salts like NaCl, the effect of the Na ion should predominate in the presence of strong anions and the effect of the Cl ion should predominate in the presence of strong cations.*

In agreement with this hypothesis it is found possible to duplicate experimentally both groups of antagonism, as defined by Loeb, i.e., NaCl is found to antagonize both anions and cations. This is not only in agreement with biological results, but it also correlates the well known fact that NaCl tends to maintain the neutrality of protein sols to which either acid or alkali have been added,[3] and to decrease the viscosity of both alike.[4]

The results of the gelatine experiments in so far as they concern antagonism are represented more completely in figure 1 in diagrammatic

form. Only a few typical electrolytes are included in the diagram, but the general principles which they exemplify are applicable to all cases thus far studied.

According to this scheme, electrolytes are found to fall into three groups.

Group I includes salts with monovalent cations and monovalent anions, the effect of the former predominating in the presence of Group II, the effect of the latter in the presence of Group III.

Group II includes alkalies and salts with bi- and trivalent anions, the effect of the anion predominating.

Group III includes acids, and salts with bi- and tri-valent cations, the effect of the cations predominating.

Members of any one group are additive to each other but antagonistic to members of either of the other two groups. In general the antagonism between Groups II and III is greater than between Groups I and II

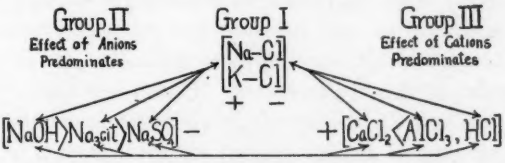

FIG. 1

Aditive combinations are bracketted together. Antagonistic combinations are connected by arrows. In general, the length of the arrows indicates the amount of antagonism expected.

or between Groups I and III. The valence of the ion (except H and OH), while not the only factor, seems of chief importance. Acids and alkalies are in general more effective than neutral salts.

An exception to this rule is found in the case of $MgCl_2$ which is found to antagonize both NaCl and $CaCl_2$. This exception, however, is in agreement with biological results.

As a criterion of antagonism, the precipitation of gelatine by 95% alcohol was used. It is found that *less alcohol is required for the precipitation of the gelatine in the presence of two antagonistic salts than when either is present alone.*

Let us for convenience designate the antagonistic salts as A and B. We find that as more and more of salt A is added to gelatine, more and more alcohol is required to produce an opaque precipitate, until finally a maximum is reached. This maximum, according to Pauli's theory,[5] corresponds to the greatest ionization of the protein and the greatest viscosity. At this point the hydration of the protein is greatest and

offers greatest resistance to the dehydration effect of the alcohol, by which precipitation is ultimately accomplished.

If now salt A be gradually replaced by an antagonistic salt B, less and less alcohol is required for precipitation until a minimum is reached. This minimum is at the isoelectric point, corresponding to greatest aggregation. *At this point, if the concentration of the salts be sufficiently high the gelatine is precipitated without alcohol.* If all of salt A be replaced by salt B, the amount of alcohol needed for precipitation again rises to the point characteristic of that salt in the concentration used. Thus an antagonism curve can be plotted, such as that shown in figure 2 for $CaCl_2$ and sodium citrate and in figure 3 for NaCl and $CaCl_2$. The probable additive effect in each figure is represented by the dotted base line. Such lines at least have resulted from similarly arranged experiments with non-antagonistic salts such as NaCl vs. KSCN and $CaCl_2$ vs. $MnCl_2$.[6]

It is frequently more convenient in determining antagonism to keep the concentration of one salt constant and gradually increase that of the other. If the two salts are *additive* to each other, the alcohol needed for precipitation is thereby *increased*. Thus when $CaCl_2$ is added to gelatine containing HCl, or when Na_2SO_4 is added to gelatine containing NaOH, the amount of alcohol needed for precipitation is increased.[7] If two *antagonistic* salts are used, on the other hand, there is a *decrease* in the amount of alcohol needed for precipitation until a minimum is reached. This is again an isoelectric point and here the gelatine may be precipitated without alcohol if the salt concentration be sufficiently high. If still more of the salt be added, there is an increase of the amount of alcohol needed for precipitation and a decrease of precipitability by salts in the absence of alcohol. Such results are observed when NaCl, for example, is added to gelatine containing HCl, NaOH, $AlCl_3$, $CaCl_2$, Na_2SO_4 or Na_3-citrate.

The molecular proportions of salts at the minimum, i.e. at the isoelectric point or point of greatest precipitability, appears to be characteristic of the particular salts used. Thus for NaCl and $CaCl_2$, it is about 100 to 20; for NaCl and $AlCl_3$, about 100 to 1.5.

Mixtures of NaCl and $AlCl_3$ in the above proportions[8] gives maximum precipitation in gelatine, milk, and olive oil emulsions.[9] Gelatine containing NaCl 0.5M shows maximum precipitation in presence of $AlCl_3$ 0.0078M and $Ce(NO)_3$ 0.00625M. The molecular proportions at these two points are 100 to 1.5 and 100 to 1.2. Mines[10] has observed a maximum precipitation of blood corpuscles in NaCl plus $CeCl_3$, the molecular proportions being between 100 to 3.3 and 100 to 0.03.

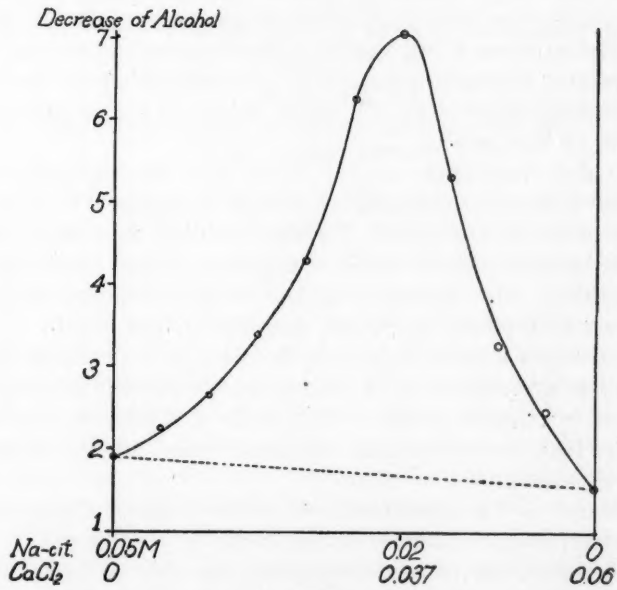

FIG. 2

Antagonism between $CaCl_2$ and Na-citrate in gelatine. Decrease of alcohol required for precipitation is plotted as ordinates (as 12 minus the number of cc. of 95% alcohol added to 5 cc. of the gelatine-salt mixtures in order to produce an opaque precipitate). As abscissae are plotted the concentrations of NaCl and $CaCl_2$ simultaneously present in the gelatine before titrating. The dotted line represents the additive effect. A pure grade of commerical gelatine was used in 3% solution. Each point represents the mean of two titrations. Each titration is accurate to 0.2 cc. The gelatine was always allowed to stand at least 15 hours in an incubator at 26°C. in order to reach equilibrium.

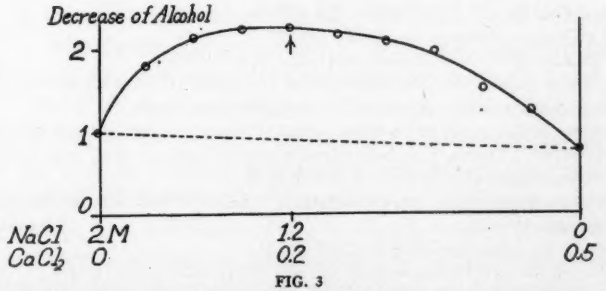

FIG. 3

Antagonism between NaCl and $CaCl_2$ in gelatine (for explanation see figure 2). At the maximum the molecular proportion of NaCl to $CaCl_2$ is 100 to 17.

In pure NaCl there was no precipitation and the corpuscles wandered to the anode. In excess of cerium there was no precipitation and the corpuscles wandered to the cathode. These results become intelligible if the point of maximum precipitation is an isoelectric point due to the predominating effect of the Cl ion (of NaCl) in the presence of the trivalent cerium cation.

From these experiments it may be reasoned that antagonistic salt solutions produce a precipitate or a state of aggregation of an isoelectric nature in protoplasm. Physicochemically, therefore, a physiologically balanced solution would be merely a mixture producing high precipitability. By varying the amount of the precipitate changes in the permeability of the protoplasm might be brought about.

In connection with the hypothesis developed here attention may be called to the suggestion of Loeb[11] that antagonism between salts and acids furnishes an excellent parallel to the results of Procter on gelatin and indicates that the protoplasmic substances which are responsible for antagonism are protein in nature.

Summary.—1. The experiments on gelatine support the hypothesis that anions antagonize cations in their effects upon organisms.

2. The hypothesis here developed resembles that of Clowes except that it requires that NaCl should antagonize any electrolyte which has either a strong anion or a strong cation.

3. The point of maximum antagonism is an isoelectric point at which the amount of alcohol needed for precipitation is at a minimum, and the aggregation or amount of precipitation is at a maximum.

[1] Loeb, These PROCEEDINGS, **1**, 473 (1915).

[2] Clowes, *J. Phys. Chem.*, **20**, 407 (1916) and *Science*, **43**, 750.

[3] Chick and Martin, *Koll.-Chem. Beihefte*, **5**, 49 (1915).

[4] Pauli, *Biochem. Zs.*, **24**, 239 (1910).

[5] Pauli, *Kolloid Zs.*, **12**, 222 (1913); **7**, 241 (1910).

[6] Pauli u. Wagner, *Biochem. Zs.*, **27**, 296 (1910).

[7] For "additive effect" see Osterhout, *Bot. Gaz.*, **58**, 178 (1914).

[8] This is true at least in low concentrations. In higher concentrations, the results are complicated by other factors and have not been fully determined.

[9] These proportions would be expected to vary with the medium used and the conditions of the experiment. Clowes (l.c.) finds that the critical point for NaCl and $CaCl_2$ in oil-water emulsions varies between 500 to 1 and 10 to 1.

[10] Clowes has shown that in critical mixtures of NaCl and $CaCl_2$, the phases of a water-oil emulsion separate out.

[10] Mines, G. R., *Koll.-Chem. Beihefte* **3**, 191 (1912).

[11] *Science*, **34**, 653 (1911); *Biochem. Zs.* **33**, 489 (1911) and **47**, 127 (1912).

SIMILARITY IN THE BEHAVIOR OF PROTOPLASM AND GELATINE

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Received by the Academy, July 28, 1916

In the course of experiments on salt antagonism in gelatin, it occurred to the writer that it would be possible to find an analogy in gelatine for the processes which occur in protoplasm when it is acted upon by antagonistic salts. These processes may be illustrated by figure 1, which shows changes in the electrical resistance of living protoplasm produced by NaCl and $CaCl_2$. If these changes are due to the diffusion of salts into the protoplasm (and the resulting increase of their concentration) it is possible that similar changes would occur in gelatine if it were divided up into small portions corresponding in size to the masses of protoplasm which form the individual living cells. The increase in the concentration of the salts as they diffused into the gelatin would produce changes in the precipitability (and other properties) of the gelatine. The manner in which the precipitability varies with the concentration of salts has been explained in the previous article.[1]

The experiments already reported[1] indicate that the favorable action of a physiologically balanced solution is due to the fact that such a solution produces a precipitate[2] (or some condition accompanying precipitation) in the protoplasm, the maximum precipitate being found at the isoelectric point. By varying the amount of this precipitate, variations in electrical resistance might be brought about.

If, however, the normal condition of protoplasm is isoelectric, the addition of *any* electrolyte would change this balance and decrease the precipitate, thus increasing permeability. It is well known, however, from Osterhout's experiments on the electrical resistance of *Laminaria*,[3] that salts like $CaCl_2$ cause a decrease of permeability at first, but this is later followed by an increase, while NaCl causes only an increase. To make the analogy between gelatine and protoplasm more complete, therefore, we should assume that the normal condition of protoplasm is somewhat on the anion side of the isoelectric point, i.e., protoplasm must bear a negative charge. The addition of $CaCl_2$ would neutralize this charge, increase the amount of precipitate or aggregation in the protoplasm and thereby decrease the permeability. In excess of Ca, however, the precipitate disappears and the permeability increases.

Figure 1 shows a set of Osterhout's electrical resistance curves for *Laminaria*, in which resistance is plotted against time. In his experiments resistance was used as a measure of permeability. From what has been said, it is to be expected that the *Laminaria* curves can be duplicated in alkaline gelatine which bears, of course, a negative charge.[4] This is done in the following way.

To a series of test tubes containing gelatine made alkaline (by adding enough NaOH to make the concentration 0.005M) is added NaCl, $CaCl_2$, or mixtures of the two, in increasing concentrations. Each tube is then titrated with 95% alcohol until an opaque precipitate is produced. Figure 2 shows the results of such an experiment. Inspection of the curves shows that low concentrations of $CaCl_2$ cause a decrease in the amount of alcohol needed for precipitation while higher concentrations cause an increase. NaCl causes only an increase. Mixtures of NaCl and $CaCl_2$ take intermediate positions. A comparison of these gelatine curves with the *Laminaria* curves in figure 1 shows a striking resemblance between the two.

In spite of the difference in the methods of obtaining the curves in protoplasm and in gelatine, the two are comparable on the assumption, that the effect of time in the *Laminaria* experiments is to increase the concentrations of the salts in the cells of the tissue. We might then suppose that variations in the concentration of the salts produced corresponding variations in the amount of a precipitate (e.g., at the plasma membrane) which offered a resistance to the passage of ions and so increased electrical resistance. This assumption would be rendered more probable if evidence were obtainable that the electrical conductivity of gelatine varies directly with the amount of alcohol required to produce precipitation. Some evidence on this point is already available.

Samec[5] working on a starch gel, measured the electrical conductivity and the alcohol precipitability simultaneously in lots of starch which had been heated for different lengths of time, and found that the two ran parallel to each other. Pauli[6] and his pupils state that the conductivity is a measure, other things being equal, of the number of electrically neutral particles present. Conductivity would therefore be least at an isoelectric point where, also, least alcohol is needed for precipitation.

There are of course quantitative discrepancies in this analogy, but one could hardly expect gelatine to be as sensitive to electrolytes as protoplasm. Qualitatively, however, the resemblance between the two curves is remarkably close, even in the following details.

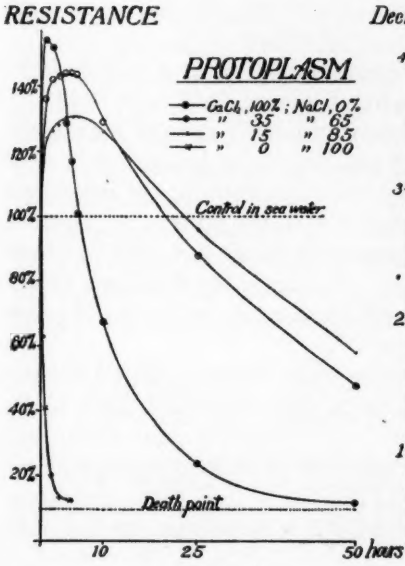

FIG. 1.

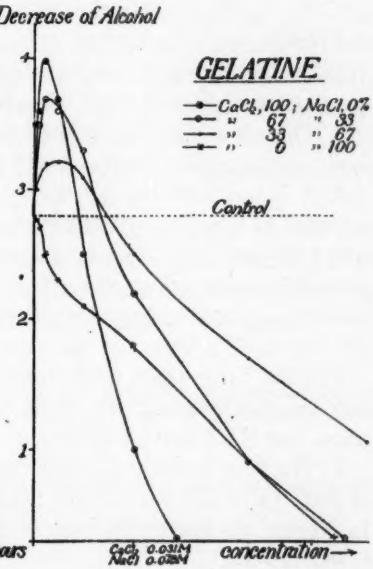

FIG. 2.

FIG. 1

Curves from Osterhout's experiments showing the changes in the electrical conductivity of protoplasm when discs of *Laminaria* are transfered from sea water to NaCl 0.52M or to $CaCl_2$ 0.27 8M or to mixtures of the two (all having the same conductivity as sea water.) Ordinates represent per cent of resistance (the resistance of the discs in sea water being taken as 100%). When the resistance has fallen to 10% of the control, the death point is reached. Here the protoplasm has the same conductivity as sea water.

FIG. 2

Curves showing how the effects of NaCl and $CaCl_2$ on the electrical resistance of protoplasm may be imitated by the effects of NaCl and $CaCl_2$ on the alcohol precipitability of gelatine (containing NaOH 0.005M). The ordinates represent the decrease (8 minus the number of cc.) of 95% alcohol required to produce an opaque precipitate, the abscissae salt concentrations. For comparison with *Laminaria* it is assumed that the salts diffuse into the gelatin (as into the protoplasm of *Laminaria*) $CaCl_2$ diffusing 80% as fast as NaCl. The molecular concentration of the NaCl solution is twice as great as that of the $CaCl_2$ solution (which is approximately the case in the *Laminaria* experiments). At the end of a given time, when the concentration of $CaCl_2$ in the gelatin is 0.031M, the concentration of NaCl will be $0.031 \times 2 \times (100 \div 80) = 0.078$M. This point is indicated in the figure. The concentrations in mixtures at this point can easily be calculated (e.g., in NaCl 50% + $CaCl_2$ 50% they would be half of those just mentioned).

It is therefore evident that we may regard the abscissae as representing time as well as concentration and that from this point of view the figure becomes comparable with figure 4, showing the changes in alcohol precipitability and in resistance which would be expected to occur with time if the salts were diffusing into the gelatin.

The last point on each curve is obtained by interpolation between the preceding point and a later one not shown in the diagram.

1. The maximum is higher in pure $CaCl_2$ than in mixtures of $CaCl_2$ and NaCl.

2. The maximum is reached slightly sooner (or at a slightly lower concentration) in pure $CaCl_2$ than in mixtures of $CaCl_2$ with NaCl.

3. There is a slight lag at the start of the NaCl curve in both *Laminaria* and gelatine. In the case of gelatine, this lag appears only if more NaOH is put into the gelatine at the start than in the experiment recorded in figure 5. With sufficient NaOH, the lag may be magnified into a distinct rise. This is in agreement with the fact, that NaCl will antagonize both anions and cations. The lag in the *Laminaria* experiments is seen in the fact that the velocity constant of the loss of resistance in NaCl is lowest at the start.[7]

The NaCl curve falls more slowly in figure 2 than in figure 1 but this may be paralleled by the results with *Rhodymenia* and other plants where the NaCl curve falls slowly.

4. The final increase in conductivity (or of alcohol) in the mixtures of NaCl and $CaCl_2$ is less rapid than in either of them taken separately. In general, the greater the percent of $CaCl_2$ in the mixture, the less rapid is the increase.

In the *Laminaria* experiments the curves approach a death point where the conductivity of the protoplasm is the same as that of sea water. No further increase of conductivity is possible. Of course this behavior would not be expected in gelatine.

In a recent article in *Science*, Spaeth[8] has presented a colloid-chemical theory of the 'vital equilibrium' of protoplasm as an explanation of Osterhout's *Laminaria* experiments. Spaeth's theory differs from that outlined above in the following fundamental points.

1. According to Spaeth the 'vital equilibrium' is between liquefying agents like NaCl and precipitating agents like $CaCl_2$. Reasoning from the gelatine analogy the equilibrium is simply between positive and negative ions.

2. Spaeth supposes that $CaCl_2$ and similar electrolytes increase the viscosity of the protoplasm by an *irreversible coagulation*, after which the viscosity becomes that of the dispersion medium, due to the complete separation of the two phases. According to the gelatine experiments, on the other hand, low concentrations of Ca cause a perfectly *reversible* precipitate, or increase of aggregation, of an isoelectric nature, which disappears gradually with excess of $CaCl_2$. Irreversible changes resulting in death appear only in much higher concentrations of $CaCl_2$.

It should be noted that the viscosity of a colloid (a conception which Spaeth uses extensively in his theory) is not a simple property of a

system but is dependent upon many different factors which may sometimes be opposing.[9] Thus Pauli and his pupils find minimum viscosity at an isoelectric point in protein sols due to minimum ionization of the protein. In the writer's gelatine experiments, however, the gelation or gelation viscosity of the gel was distinctly at a maximum at the isoelectric point due to maximum aggregation. It appears necessary to distinguish between these two kinds of viscosity.

Summary.—A close analogy to Osterhout's experiments on the electrical resistance of *Laminaria* is found in gelatine (plus NaOH), if we assume that the effect of time in the *Laminaria* experiments is to increase the concentrations of the salts in the cells of the tissue.

[1] These PROCEEDINGS, **2**, 534 (1916).

[2] For the sake of brevity the word precipitate is used throughout to denote not only an actual precipitate, but any accompanying conditions which vary with the amount of precipitate or the degree of precipitability.

[3] Cf. Osterhout, *Science*, **41**, 255 (1915) for summary of results.

[4] Pauli has concluded for other reasons that protoplasm reacts much like protein soils containing alkali. *Biochem. Zs.*, **24**, 239 (1910).

[5] Samec, *Koll.-Chem. Beihefte*, **5**, 141 (1913).

[6] Pauli, loc. cit.

[7] Osterhout, *Science*, **39**, 544 (1914).

[8] Spaeth, *Science*, **43**, 502 (1916).

[9] Ostwald, *Kolloid. Zs.*, **12**, 213 (1913).

ON CERTAIN ASYMPTOTIC EXPRESSIONS IN THE THEORY OF LINEAR DIFFERENTIAL EQUATIONS

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Received by the Academy, July 6, 1916

The nature of the solutions of a certain linear differential equation containing a complex parameter has been investigated by Prof. G. D. Birkhoff,[1] who discovered the asymptotic character of the solutions when the parameter is large in absolute value. These results he employed in the study of expansion problems connected with the particular differential equation

$$\frac{d^n u}{dx^n} + P_2(x)\frac{d^{n-2}u}{dx^{n-2}} + \ . \ . \ . \ + P_n(x)\,u + \rho^n u = 0, \qquad (1)$$

together with n linearly independent linear boundary conditions

$$W_1(u) = 0,\ W_2(u) = 0,\ \ldots,\ W_n(u) = 0. \qquad (2)$$

It is the aim of this paper to present asymptotic formulas for n linearly independent solutions $y_1, y_2, \ldots, y_n$ of equation (1) which are in

some respects more precise than those obtained by Birkhoff, and also to present similar asymptotic formulas for the n functions $\bar{y}_1, \bar{y}_2, \ldots, \bar{y}_n$, related to the n y's by the n identities

$$\sum_{i=1}^{n} y_i^{(k)} \bar{y}_i = \begin{cases} 0, & k = 0, \ldots, n-2, \\ 1, & k = n-1. \end{cases} \tag{3}$$

These functions $\bar{y}$ play an important rôle in the theory of linear differential equations. As is well known, they form a system of linearly independent solutions of the equation adjoint to equation (1), while the expression

$$\sum_{i=1}^{n} y_i(x)\, \bar{y}_i(t)$$

is of fundamental importance in Lagrange's method of solving the non-homogeneous equation of which (1) is the reduced equation, as well as in the formation of the Green's function of the system (1) and (2). Asymptotic forms for the $\bar{y}$'s were also used by Birkhoff in his paper on expansion problems.[2]

I was led to make refinements in the forms of the y's and the $\bar{y}$'s in connection with a paper treating the degree of convergence of the expansion associated with the differential system (1) and (2).

Birkhoff divided the plane of the complex parameter ρ into $2n$ equal sectors,

$$S_k : k\pi/n \leqq \arg \rho \leqq (k+1)\pi/n, \quad k = 0, 1, \ldots, 2n-1,$$

and then numbered the n n-th roots of -1, $w_1, w_2, \ldots, w_n$, in such a manner that when ρ is on any given sector S_k, the inequalities

$$R(\rho w_1) \leqq R(\rho w_2) \leqq \ldots \leqq R(\rho w_n)$$

are satisfied, where $R(\rho w_i)$ denotes the real part of ρw_i. He then proved that if the coefficients $P_s(x)$ in (1) have continuous derivatives of all orders in the closed interval $a \leqq x \leqq b$, there exist for ρ in any given S_k n independent solutions of (1),

$$\begin{aligned} y_i &= u_i(x, \rho) + e^{\rho w_i (x-c)} E_{i0}/\rho^{n+1}, \\ y_i^{(k)} &= u_i^{(k)}(x, \rho) + e^{\rho w_i (x-c)} E_{ik}/\rho^{n+1-k}, \\ i &= 1, 2, \ldots, n; \; k = 1, 2, \ldots, n-1, \end{aligned} \tag{4}$$

in which

$$u_i(x, \rho) = e^{\rho w_i (x-c)} \left[1 + \frac{u_{i1}(x)}{\rho} + \ldots + \frac{u_{in+1}(x)}{\rho^{n+1}} \right],$$

where m is any positive integer or zero.[3] The E_{ij} are functions of x and ρ which are bounded for x in (a, b) and for ρ in S_k and large in absolute value. The y_i are analytic in ρ in S_k, and the $u_{ij}(x)$ have derivatives of all orders with respect to x in (a, b).

The modification here proposed is this: *If the coefficients $P_s(x)$ have continuous derivatives of order $(m + n - s)$ in (a, b), m being any positive integer or zero, then there exist n solutions of (1) of the form (4), analytic in ρ in the sector S_k, and the functions $u_i(x,\rho)$ are of the form*

$$u_i(x, \rho) = e^{\rho w_i (x-c)} [1 + \varphi_1(x)/\rho w_i + \ . \ . \ . \ + \varphi_m(x)/(\rho w_i)^m],$$

where the functions $\varphi_j(x)$ have continuous derivatives of order $(m + n - j)$, and are independent of i.

The improvement in precision over Birkhoff's formulas consists primarily in putting the $u_i(x,\rho)$ in the form indicated, where the $\varphi_j(x)$ are independent of i; the details concerning the number of derivatives of the P's and the φ's are of secondary importance. A similar remark applies to the statement concerning the $\bar{y}$'s, which is as follows:

The n functions $\bar{y}_i$, determined by the n equations (3), have when $|\rho|$ is large the asymptotic form

$$\bar{y}_i = \frac{e^{-\rho w_i (x-c)}}{n(\rho w_i)^{n-1}} [v_i(x, \rho) + \bar{E}_i/\rho^{m+1}], \quad i = 1, 2, \ . \ . \ . \ , n,$$

where

$$v_i(x, \rho) = 1 + \psi_1(x)/\rho w_i + \ . \ . \ . \ + \ \psi_m(x)/(\rho w_i)^m,$$

in which the functions $\psi_j(x)$ are independent of i and have continuous $(m + n - j)$-th derivatives in (a, b).

The proof of the asymptotic formulas for the y's is simply an adaptation of the proof given by Birkhoff. In the case of the $\bar{y}$'s, we verify the formulas by substituting the values of the $\bar{y}_i$ given above into equations (3) and showing that the ψ's and E's with the desired properties can be chosen to satisfy them.

[1] *Trans. Amer. Math. Soc.*, 9, 219–231, 373–395 (1908).

[2] Loc. cit., p. 391, formula (56).

[3] For the formulas here quoted see loc. cit., pp. 381–2, formulas (21) and (23). They are quoted in (4) with some slight changes.

ON NEWTON'S METHOD OF APPROXIMATION

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Received by the Academy, August 8, 1916

In the first of the following theorems[1] a condition is given under which Newton's method of approximation for computing a real root of an equation $f(x)=0$ and the extension of this method used in computing a real solution of a system of equations $f_i(x_1, x_2, \ldots, x_n)=0$, $(i=1, 2, \ldots, n)$, will with certainty lead to such a root or solution. The condition relates to the absolute value of $f(x)$ or of the functions $f_i(x_1, x_2, \ldots, x_n)$ corresponding to the initial values of x and of the variables $x_1, x_2, \ldots, x_n$ respectively. No assumption is made as to the existence of a solution. On the contrary it is proved that under the condition to which reference has been made one and but one solution exists in a certain designated neighborhood of the initial x or $(x_1, x_2, \ldots, x_n)$. The second theorem is the extension of the first (for $n=1$) to the case of a complex root of an analytic equation $f(z) = 0$.

Theorem 1. *Let $f_i(x_1, x_2, \ldots, x_n)$, $(i = 1, 2, \ldots, n)$, be a system of real functions of the real variables $x_1, x_2, \ldots, x_n$ which have continuous first and second derivatives in the region R, $(x_1^{(0)}, x_2^{(0)}, \ldots, x_n^{(0)})$ a set of values of $x_1, x_2, \ldots, x_n$ belonging to this region, and $\xi_1, \xi_2, \ldots, \xi_n$ the set of numbers determined by the equations.*

$$f_i(x_1^{(0)}, x_2^{(0)}, \ldots, x_n^{(0)}) + \sum_{k=1}^{n} \frac{\partial f_i}{\partial x_k^{(0)}} \xi_k = 0 \qquad (i = 1, 2, \ldots, n)$$

and let S denote the interval, circle, sphere, or hypersphere whose center is $(x_1^{(0)} + \xi_1, \ldots, x_n^{(0)} + \xi_n)$ and whose radius is $\rho = \left(\sum_{k=1}^{n} \xi_k^2\right)^{\frac{1}{2}}$, S_ρ being supposed to belong to R.

Suppose also that in S the functional determinant F of the functions f_i does not vanish, $\mu(<\infty)$ is the upper bound of the absolute values of the fractions whose denominators are F and whose numerators are the several first minors of F, and $\nu(<\infty)$ is the upper bound of the absolute values of the second derivatives of the functions f_i.

Then, if

$$\left[\sum_{i=1}^{n} \left\{ f_i(x_1^{(0)}, x_2^{(0)}, \ldots, x_n^{(0)}) \right\}^2\right]^{\frac{1}{2}} < \frac{1}{n^{7/2}\mu^2\nu} \qquad (a)$$

the equations $f_i = 0$ have one and but one solution in S, and an approximate value of this solution, as close as may be desired, will be obtained by determinations first of $\xi_1^{(j)}, \xi_2^{(j)}, \ldots, \xi_n^{(j)}$ and then of $x_1^{(j+1)}, x_2^{(j+1)}, \ldots, x_n^{(j+1)}$, for $j = 0, 1, 2 \ldots$ successively, by the equations

$$\left.\begin{aligned} f_i\,(x_1^{(j)}, x_2^{(j)}, \ldots, x_n^{(j)}) + \sum_{k=1}^{n} \frac{\partial f_i}{\partial x_k^{(j)}}\,\xi_k^{(j)} = 0, \qquad & (i = 1, 2, \ldots, n) \\ x_k^{(j+1)} = x_k^{(j)} + \xi_k^{(j)}, \qquad & (k = 1, 2, \ldots, n), \end{aligned}\right\} \tag{b}$$

(where $\xi_k^{(0)} = \xi_k$), the solution being $\lim_{j=\infty} (x_1^{(j)}, x_2^{(j)}, \ldots, x_n^{(j)})$.

Moreover the equations (b) will yield a similar sequence of approximations to this solution if instead of $(x_1^{(0)}, x_2^{(0)}, \ldots x_n^{(0)})$ any other point in S be chosen as the point of departure.

For the case of a single equation $f(x) = 0$ the condition (a) reduces to

$$|f(x_0)| < \frac{\lambda^2}{\nu}, \tag{a'}$$

where $\lambda\,(>0)$ is the lower bound in the interval S of the values of $|f'(x)|$.

For let

$$f_i^{(j)} = f_i\,(x_1^{(j)}, x_2^{(j)}, \ldots, x_n^{(j)}), \quad \varphi_j = \left\{\sum_{i=1}^{n} [f_i^{(j)}]^2\right\}^{\frac{1}{2}}, \quad \rho_j = \left\{\sum_{k=1}^{n} [\xi_k^{(j)}]^2\right\}^{\frac{1}{2}}.$$

Then, if both $(x_1^{(j)}, x_2^{(j)}, \ldots, x_n^{(j)})$ and $(x_1^{(j+1)}, x_2^{(j+1)}, \ldots, x_n^{(j+1)})$ are in S,

$$f_i^{(j+1)} = f_i^{(j)} + \sum_{k=1}^{n} \frac{\partial f_i}{\partial x_k^{(j)}}\,\xi_k^{(j)} + \tfrac{1}{2} \sum_{k,l=1}^{n} \frac{\partial^2 f_i}{\partial x_k^{(j_i)}\,\partial x_l^{(j_i)}}\,\xi_k^{(j)}\,\xi_l^{(j)}, \quad (i = 1, 2, \ldots, n), \tag{1}$$

where each $x_k^{(j_i)}$ lies between $x_k^{(j)}$ and $x_k^{(j+1)}$.

Hence if the numbers $\xi_k^{(j)}$ be so taken as to satisfy the equations

$$f_i^{(j)} + \sum_{k=1}^{n} \frac{\partial f_i}{\partial x_k^{(j)}}\,\xi_k^{(j)} = 0, \quad (i = 1, 2, \ldots, n), \tag{2}$$

we shall have

$$f_i^{(j+1)} = \tfrac{1}{2} \sum_{k,l=1}^{n} \frac{\partial^2 f_i}{\partial x_k^{(j_i)}\,\partial x_l^{(j_i)}}\,\xi_k^{(j)}\,\xi_l^{(j)}, \quad (i = 1, 2, \ldots, n), \tag{3}$$

Solving the equations (2), we find

$$\xi_k^{(j)} = -\frac{\sum_{i=1}^{n} A_{ik}^{(j)} f_i^{(j)}}{F_j}, \quad (k = 1, 2, \ldots, n), \tag{4}$$

where F_j is the value of F for $(x_1, x_2, \ldots, x_n) = (x_1^{(j)}, x_2^{(j)}, \ldots x_n^{(j)})$, and $A_{ik}^{(j)}$ the cofactor of the element in the ith row and the kth column of F_j. But

$$\left| \sum_{i=1}^{n} A_{ik}^{(j)} f_i^{(j)} \right| \leqq \left\{ \sum_{i=1}^{n} [A_{ik}^{(j)}]^2 \right\}^{\frac{1}{2}} \left\{ \sum_{i=1}^{n} [f_i^{(j)}]^2 \right\}^{\frac{1}{2}}$$

Hence

$$\rho_j^2 \leqq \frac{\sum_{i,k=1}^{n} [A_{ik}^{(j)}]^2}{F_j^2} \sum_{i=1}^{n} [f_i^{(j)}]^2 \leqq n^2 \mu^2 \phi_j^2$$

and therefore

$$\rho_j \leqq n \mu \phi_j. \tag{5}$$

Again, the expressions under the summation sign in the equations (3) are of the form

$$\sum_{k,l=1}^{n} a_{kl} \xi_k \xi_l$$

and

$$\left| \sum_{k,l=1}^{n} a_{kl} \xi_k \xi_l \right| = \left| \sum_{k=1}^{n} \left(\sum_{l=1}^{n} a_{kl} \xi_l \right) \xi_k \right| \leqq \left\{ \sum_{k=1}^{n} \left(\sum_{l=1}^{n} a_{kl} \xi_l \right)^2 \right\}^{\frac{1}{2}} \left\{ \sum_{k=1}^{n} \xi_k^2 \right\}^{\frac{1}{2}}$$

$$\leqq \left(\sum_{k,l=1}^{n} a_{kl}^2 \right)^{\frac{1}{2}} \sum_{k=1}^{n} \xi_k^2 \leqq na \sum_{k=1}^{n} \xi_k^2, \tag{6}$$

where a denotes the greatest of the numbers $|a_{ik}|$.

Hence

$$\varphi_{j+1}^2 \leqq n \left(\frac{n\nu}{2} \right)^2 \left\{ \sum_{k=1}^{n} [\xi_k^{(j)}]^2 \right\}^{\frac{1}{2}} \leqq \frac{n^3 \nu^2}{2^2} \rho_j^4$$

and therefore

$$\varphi_{j+1} \leqq \frac{n^{3/2} \nu}{2} \rho_j^2. \tag{7}$$

From (5) and (7) it follows that

$$\varphi_{j+1} \leqq k_1 \phi_j^2, \text{ where } k_1 = \frac{n^{7/2} \mu^2 \nu}{2}, \tag{8}$$

$$\rho_{j+1} \leqq k_2 \rho_j^2, \text{ where } k_2 = \frac{k_1}{n\mu} = \frac{n^{5/2} \mu \nu}{2} \tag{9}$$

Hence $k_1 \varphi_{j+1} \leqq (k_1 \varphi_j)^2$ and therefore, by setting $j = 0, 1, 2, \ldots$ successively,

$$k_1 \varphi_j \leqq (k_1 \phi_0)^{2^j}. \tag{10}$$

Similarly

$$k_2 \rho_j \leqq (k_2 \rho)^{2^j}, \tag{11}$$

Let r denote any positive number less than 1, and suppose that $k_1 \varphi_0 < r$. Then since, by (5), $\rho \leqq n \mu \phi_0$, we also have $k_2 \rho < r$, and therefore, by (8) and (9),

$$k_2 \varphi_j < r^{2^j}, \qquad k_2 \rho_j r^{2^j}. \tag{12}$$

Again $\rho_{j+1} \leqq k_2 \rho_j \rho_j$ and therefore

$$\rho_{j+1} < r^{2^j} \rho_j. \tag{13}$$

Also, $k_2 \rho_j \leqq k_2 \rho (k_2 \rho)^{2^j - 1}$ and therefore

$$\rho_j < r^{2^j - 1} \rho. \tag{14}$$

Therefore, since $r < 1$, the sum $\rho_1 + \rho_2 \ldots \rho_j$ increases with j to a limit which is less than $\rho r / (1 - r^2)$.

But $\rho r / (1 - r^2) < \rho$ when $r \leqq 1/2$.

Therefore when $r = 1/2$, that is when the condition $k_1 \varphi_0 < r$ becomes

$$\varphi_0 < \frac{1}{2k_1} = \frac{1}{n^{7/2} \mu^2 \nu}, \tag{15}$$

the point whose coordinates are $x_k^{(j)} = (x_k^{(0)} + \xi_k^{(0)}) + \xi_k^{(1)} + \ldots + \xi_k^{(j-1)}$, $(k = 1, 2, \ldots, n)$, will remain in S as j increases and will approach a definite limiting position $(c_1, c_2, \ldots, c_n)$ in S as $j = \infty$. Moreover by (12), $\lim_{j=\infty} \varphi_j = 0$, and therefore, since the functions f_i are continuous, $f_i (c_1, c_2, \ldots c_n) = 0$, $(i = 1, 2, \ldots n)$. Therefore the equations $f_i = 0$ have the solution $(c_1, c_2, \ldots c_n)$ in S.

Observe that it follows from (5) that when (15) is satisfied,

$$\rho < \frac{1}{2k_2} = \frac{1}{n^{5/2} \mu \nu} \tag{16}$$

The equations $f_i = 0$ have no other solution than $(c_1, c_2, \ldots c_n)$ in S. For suppose that $(c_1 + h_1, \ldots, c_n + h_n)$ represents another such solution. Then by developing as in (1) and applying (6)

$$0 = \sum_{k=1}^{n} \frac{\partial f_i}{\partial c_k} h_k + \frac{\theta_i}{2} n \nu \sum_{k=1}^{n} h_k^2, \quad (i = 1, 2, \ldots, n), \tag{17}$$

where $|\theta_i| \leqq 1$.

Solving these equations for the numbers h_k in terms of $\sum_{k=1}^{n} h_k^2$, we obtain, by the method used in deriving (5) from (2),

$$\left[\sum_{k=1}^{n} h_k^2\right]^{\frac{1}{2}} \leqq \frac{n^{5/2}\mu\nu}{2} \sum_{k=1}^{n} h_k^2,$$

and therefore, if $\sum_{k=1}^{n} h_k^2 \neq 0$,

$$\left[\sum_{k=1}^{n} h_k^2\right]^{\frac{1}{2}} \geqq \frac{2}{n^{5/2}\mu\nu} > 2\rho. \tag{18}$$

Hence $(c_1 + h_1, \ldots, c_n + h_n)$ lies outside of S. Therefore the existence of a second solution in S is impossible.

The equations (b) will also yield a sequence of approximations to $(c_1, c_2, \ldots, c_n)$ similar to the sequence $(x_1^{(j)}, x_2^{(j)}, \ldots x_n^{(j)})$ if instead of $(x_1^{(0)}, x_2^{(0)}, \ldots x_n^{(0)})$ any other point in S be taken as the point of departure. For let $(a_1^{(0)}, a_2^{(0)}, \ldots, a_n^{(0)})$ be any point in S, and $\xi_k^{(j)}$, $a_k^{(j+1)}$, $d_k^{(j)}$, $(k = 1, 2, \ldots, n)$, the numbers determined by the equations

$$f_i(a_1^{(j)}, a_2^{(j)}, \ldots, a_k^{(j)}) + \sum_{k=1}^{n} \frac{\partial f_i}{\partial a^{(j)}} \xi_k^{(j)} = 0, \quad (i = 1, 2, \ldots, n),$$

$$a_k^{(j+1)} = a_k^{(j)} + \xi_k^{(j)}, \quad d_k^{(j)} = c_k - a_k^{(j)}, \qquad (k = 1, 2, \ldots, n),$$

for $j = 0, 1, 2, \ldots$ successively.

Then since

$$c_k = a_k^{(j)} + d_k^{(j)} = a_k^{(j)} + (\xi_k^{(j)} + d_k^{(j+1)}), \quad (k = 1, 2, \ldots, n),$$

we shall have, on developing as in (1) and taking into account the equations which determine the numbers $\xi_k^{(j)}$,

$$0 = \sum_{k=1}^{n} \frac{\partial f_i}{\partial a_k^{(j)}} d_k^{(j+1)} + \tfrac{1}{2} \sum_{k,l=1}^{n} \frac{\partial^2 f_i}{\partial x_k^{(j_i)} \partial x_l^{(j_i)}} d_k^{(j)} d_l^{(j)}, \ (i = 1, 2, \ldots, n), \tag{19}$$

where each $x_k^{(j_i)}$ lies between $a_k^{(j)}$ and c_k, $(k = 1, 2, \ldots . n)$.

From (19) it follows, as in the proof of (5), that

$$\delta_{j+1} \leqq k_2 \delta_j^2, \tag{20}$$

where $\delta_j = \left\{\sum_{k=1}^{n} [d_k^{(j)}]^2\right\}^{\frac{1}{2}}$ and, as above, $k_2 = n^{5/2}\mu\nu/2$.

From (20) in turn it follows, as in (10), that

$$k_2 \delta_j \leqq (k_2 \delta_0)^{2^j}; \tag{21}$$

therefore, if $k_2 \delta_0 < 1$, that $\lim_{j=\infty} \delta_j = 0$ and $\lim_{j=\infty} (a_1^{(j)}, a_2^{(j)}, \ldots, a_n^{(j)}) = (c_1, c_2, \ldots, c_n)$.

But δ_0 is the distance of the point $(a_1^{(0)}, a_2^{(0)}, \ldots, a_n^{(0)})$ from the point $(c_1, c_2, \ldots, c_n)$, and $k_2\delta_0 < 1$ if $\delta_0 < 1/k_2$; therefore, by (16), if

$\delta_0 < 2\rho$. And the condition $\delta_0 < 2\rho$ is satisfied if $(a_1^{(0)}, a_2^{(0)}, \ldots, a_n^{(0)})$ be taken anywhere in S.

Again since $k_2\,\delta_0 = r < 1$ we have, as in (12), $\delta_{j+1} \leqq (k_2\,\delta_j)\,\delta_j \leqq r^{2^j}\,\delta_j < \delta_j$. Hence each approximation in the sequence $(a_1^{(j)}, a_2^{(j)}, \ldots, a_n^{(j)})$, $(j = 0, 1, 2, \ldots)$, is closer than the one which precedes it.

Finally, by (21), $\delta_j \leqq r^{2^j}/k_2$. Let j' be any value of j such that $r^{2^{j'}}/k_2 < 0.1$ and $r^{2^{j'}} < 0.1$ and set $j = j' + l$ $(l = 0, 1, 2, \ldots)$. We then have

$$\delta_{j'+l} \leqq \frac{r^{2^{j'+l}}}{k_2} = \frac{r^{2^{j'}}}{k_2}\,(r^{2^{j'}})^{2^l - 1} < (0.1)^{2^l}.$$

Hence $\left\{\sum_{k=1}^{n} [a_k^{j'+l}]^2\right\}^{\frac{1}{2}}$ will coincide with $\left\{\sum_{k=1}^{n} c_k^2\right\}^{\frac{1}{2}}$ and therefore $a_k^{j'+l}$ with c_k $(k = 1, 2, \ldots, n)$, to at least the 2^lth decimal figure.

Theorem 2. *Let $f(z)$ be any function of the complex variable z which is analytic at $z = z_0$, and h the number determined by the equation*

$$f(z_0) + f'(z_0)\,h = 0.$$

Let S be the circular region whose center is $z_0 + h$ and whose radius is $\rho = |h|$, and suppose that, in S, $f(z)$ is everywhere analytic, $\lambda\,(>0)$ is the lower bound of the values of $|f'(z)|$ and $\nu\,(<\infty)$ is the upper bound of the values of $|f''(z)|$. Then, if

$$|f(z_0)| < \frac{\lambda^2}{\sqrt{2}\,\nu}, \qquad (a'')$$

the equation $f(z) = 0$ has one and but one root in S, and this root will be approximated to uninterruptedly by successive determinations of h_j and z_{j+1} by the formulas

$$f(z_j) + f'(z_j)\,h_j = 0, \quad z_{j+1} = z_j + h_j, \quad (j = 0, 1, 2, \ldots), \qquad (b')$$

(where $h_0 = h$), the root being $\lim_{j=\infty} z_j$.

For let

$$z_j = x + iy, \quad f(z_j) = \varphi(x, y) + i\,f(x, y), \quad h_j = \xi + i\,\eta.$$

Then if z_j and z_{j+1} are in S, we shall have

$$f(z_j + h_i) = f(z_j) + f'(z_j)\,h_j + \tfrac{1}{2}\left(\frac{\partial^2\varphi}{\partial x'^2}\,\xi^2 + 2\,\frac{\partial^2\varphi}{\partial x'\,\partial y'}\,\xi\eta + \frac{\partial^2\varphi}{\partial y'^2}\,\eta^2\right)$$
$$+ \frac{i}{2}\left(\frac{\partial^2\psi}{\partial x''^2}\,\xi^2 + 2\,\frac{\partial^2\psi}{\partial x''\,\partial y''}\,\xi\eta + \frac{\partial^2\psi}{\partial y''^2}\,\eta^2\right) \qquad (22)$$

where x', x'' lie between x and $x + \xi$; y', y'' between y and $y + \eta$. But

$$\left|\frac{\partial^2\varphi}{\partial x'^2}\xi^2+2\frac{\partial^2\varphi}{\partial x'\partial y'}\xi\eta+\frac{\partial^2\varphi}{\partial y'^2}\eta^2\right|=\left|\frac{\partial^2\varphi}{\partial x'^2}(\xi^2-\eta^2)-2\frac{\partial^2\psi}{\partial x'^2}\xi\eta\right|$$

$$\leqq\left\{\left[\frac{\partial^2\varphi}{\partial x'^2}\right]^2+\left[\frac{\partial^2\psi}{\partial x'^2}\right]^2\right\}^{\frac{1}{2}}\left\{(\xi^2-\eta^2)^2+4\xi^2\eta^2\right\}^{\frac{1}{2}}\leqq\nu|h_j|^2.$$

Similarly

$$\left|\frac{\partial^2\psi}{\partial x''^2}\xi^2+2\frac{\partial^2\psi}{\partial x''\partial y''}\xi\eta+\frac{\partial^2\psi}{\partial y''^2}\eta^2\right|\leqq\nu|h_j|^2.$$

Therefore

$$f(z_j+h_j)=f(z_j)+f'(z_j)\,h_j+\frac{\theta_1+i\theta_2}{2}\nu|h_j|^2,\quad -1<\theta_1,\theta_2<1,\quad(23)$$

Hence if h_j be so taken as to satisfy the equation $f(z_j)+f'(z_j)\,h_j=0$ and if, as in the proof of Theorem 1, we set $|h_j|=\rho_j$, $|f(z_j)|=\phi_j$, we shall have

$$\rho_j\leqq\frac{1}{\lambda}\varphi_j,\qquad\varphi_{j+1}\leqq\frac{\sqrt{2}\,\nu}{2}\rho_j^2.$$

But these are the same as the inequalities (5) and (7) in the proof of Theorem 1 for the case $n=1$ except that ν is here replaced by $\sqrt{2}\nu$. It therefore at once follows from that proof, and in particular from the inequalities (15) and (18), that if $\varphi_0<\lambda^2/\sqrt{2}\nu$ and therefore $\rho=\rho_0<\lambda/\sqrt{2}\nu$, the equation $f(z)=0$ has one and but one root is S; also that the equations (b)′ will yield a sequence of approximations to the root if instead of z_0 any other point in S be taken as the point of departure.[2]

[1] This paper was read before the American Mathematical Society, April 29, 1916.

[2] The distinctive feature of the method used in this paper is the determination of a number C such that if $\varphi_0<C$, then $\lim_{j=\infty}\varphi_j=0$. In this respect it differs from other discussions of Newton's method which I have been able to find. Of such discussions the following should be mentioned. Cauchy (Oeuvres [Ser. 2, Vol. 4], p. 573) obtained $\rho<\lambda/2\nu$ as the condition for the existence in S of a real root of a real equation obtainable by Newton's method, and $\rho<\lambda/4\nu$ as the corresponding condition for a complex root. Quite recently G. Faber (*J. Math., Berlin*, 138) has proved, for an analytic equation $f(z)=0$, that if $|f(z)f''(z)/[f'(z)]^2|<\alpha<1$ in the circle whose center is z_0 and radius $\rho/(1-\alpha)$, a root of $f(z)=0$, obtainable by Newton's method, exists in this circle. I have been unable to discover any previous proofs of the existence of a solution for the case $n>1$. But Runge (*Encyc. Math. Wiss.*, 1, p. 446) and E. Blutel (*Paris, Acad. Sci.*, C. R. 151, 1109) have given proofs that if a solution exists at a certain point C, there must also exist a region R about C from any point of which a steady approach to C will be made by Newton's method Blutel's method of proof (an extension of one employed by Cauchy) being that which I have used in the proof of the corresponding part of Theorem 1.